

Additives for Processing Plastics

Field of the Invention

This invention relates to additives for the processing of plastics, the additives being present in a granular supply form, characterized in that the granules are present in the form of spherical to cylindrical granules with a
5 length-to-diameter ratio of 1:1 to 3:1. The invention also relates to compositions containing such granules for the processing of plastics and to the use of the granules as auxiliaries for the processing of plastics.

Prior Art

Sub A1
10 Plastics are polymers which consist structurally of molecule chains with numerous, almost infinitely recurring structural elements and which differ in their physical properties from low molecular weight compounds. Thus, polymers have high tensile strengths and elasticity, for example, by comparison with low molecular weight compounds.

15 In the course of industrial processing, suitable additives are incorporated in polymerized plastic melts to facilitate their further processing and their intended application. In this way, basic polymers can be adapted to meet individual requirements in regard to the required properties.

20 Additives for plastics are available in various supply forms. For solid compounds, the simplest supply form is the powder. Unfortunately, **powder** can cake too easily and leads to dust emissions during processing. Compression of the powder in a granulator gives **rodlet granules**. Although the dust component is small, processing problems can be caused
25 by the poorer handling behavior of such granules and the dust present. For some additives which have a high meltable component, **pellets** or **flakes** are available as supply forms. For production, the particular product

is melted and then cooled down on cooled flaking rollers or belts. Pellets are dust-free and may readily be incorporated in the plastic. However, thermally labile or reactive compounds cannot be flaked or pelleted.

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Description of the Invention

The problem addressed by the present invention was to provide additives for the processing of plastics which would be easy to handle and which could readily be incorporated in thermoplastics.

It has now been found that extruded plastic additives can be converted by spheronizing, such as "marumerizing", into a substantially spherical or cylindrical shape. Granules thus shaped ("**beads**") on the one hand afford the advantage of easy handling and freedom from dust; on the other hand, they can readily be incorporated during the processing of thermoplastics, i.e. dispersed in the plastics.

The additive beads thus produced are eminently suitable as a supply form for plastic additives, more particularly for stabilizer and/or lubricant compounds for the processing of PVC, for example those based on calcium/zinc and on lead.

The present invention relates to additives for the processing of plastics, the **additives being present in a granular supply form**, characterized in that the granules are present in the form of spherical or cylindrical granules with a length-to-diameter ratio of 1:1 to 3:1.

With regard to the length-to-diameter ratio, attention is drawn to the following: the additives granules according to the invention assume the form of bodies of rotation (i.e. they may also be graphically referred to as "beads"). The length of the longitudinal axis of the beads is termed the "length" while the maximum diameter of the beads (as measured perpendicularly of the longitudinal axis) is termed the "diameter". In cases where the length-to-diameter ratio is 1:1, the beads are spheres. In the process described hereinafter for producing the additive granules, the bead

form is obtained by virtue of the fact that, after extrusion and chopping up of the extruded strands at the granulation head with multiple-bore dies, cylindrical particles are initially obtained and are then rounded off at their ends in spheronizing machines.

5 The supply form according to the invention for the plastic additives combines several favorable applicational properties which are not found in this number in conventional supply forms, such as powders or pellets. For experimental proof, reference is made to the Examples. As mentioned above, these positive applicational properties include excellent transport
10 behavior and the absence of dust - both properties which guarantee excellent handling behavior. In addition, the supply form according to the invention opens up extensive possibilities in regard to the "range of formulation". By this is meant that the beads according to the invention may contain not just one additive, but also several additives irrespective of
15 whether these additives are - for instance - thermally labile, infusible or substantially infusible, represent otherwise difficult-to-handle polymers, etc. The positive applicational properties mentioned remain intact even when the formulation range of the beads according to the invention is broad, i.e. when several different additives, including thermally labile and otherwise
20 difficult-to-handle additives, are present in the beads.

According to the invention, the **plastics** may be selected basically as required from the thermoplastics known to the relevant expert. The following are examples of suitable plastics:

- homopolymers of an α -olefin containing two to eight carbon atoms,
25 copolymers of two corresponding α -olefins, preferably copolymers of ethylene, ethylene homopolymers, such as HDPE (high-density polyethylene), LDPE (low-density polyethylene), VLDPE (very low-density polyethylene), LLDPE (linear low-density polyethylene), MDPE (medium-density polyethylene), UHMPE (ultra-high-molecular
30 polyethylene), VPE (crosslinked polyethylene), HPPE (high-pressure

polyethylene), isotactic polypropylene, syndiotactic polypropylene, Metallocen-catalyzed polypropylene, high-impact polypropylene, random copolymers based on ethylene and propylene, block copolymers based on ethylene and propylene, homopolymers based on 1-butylene, 1-pentylene, 1-hexylene, 1-octylene, isobutylene, 2-methyl-1-butylene, 3-methyl-1-pentylene, 4-methyl-1-pentylene, 2,3-dimethyl-1-butylene, 2-ethyl-1-butylene and mixtures thereof.

- copolymers of ethylene with 1-butylene, 1-hexylene, 1-octylene and 4-methyl-1-pentylene.
- ethylene/vinyl acetate copolymers, ethylene/ethyl acetate copolymers, ethylene/acrylic acid copolymers and mixtures thereof.
- ethylene/propylene rubber (EPDM), including diene-modified types (EPR), styrene/butadiene/styrene copolymers (SBS), styrene/ethylene/butylene/styrene copolymers (SEBS) and mixtures thereof.
- halogen-containing plastics, more particularly homopolymers of vinyl compounds, for example vinyl chloride.

According to the invention, the **additives** may be selected basically as required from the additives known to the relevant expert for the processing of thermoplastics. Examples of suitable additives are antistatic agents, antifogging agents, antioxidants, UV stabilizers, coupling agents, calendering aids, mold release agents, lubricants, release agents, slip agents, plasticizers, perfumes, flame retardants, fillers and agents for increasing thermal stability (heat stabilizers).

So far as the terms "lubricants" and "release agents" are concerned, attention is drawn to the following: in the standard language of the expert, release agents are products which reduce the frictional resistances primarily between the polymer melt and the steel surface of the machine used for molding; the effect of reducing the frictional resistance is that the

melt pressure of the melt is reduced. By contrast, lubricants act predominantly in the polymer melt and reduce the internal frictional forces so that, even with high filler contents, the melt retains good plastic flow which is important for filling the mold.

5 In one embodiment of the invention, calcium salts and/or magnesium salts and/or aluminium salts and/or zinc salts solid or liquid at 20°C selected from

- a) calcium salts of saturated or unsaturated, linear or branched monocarboxylic acids containing 6 to 36 carbon atoms,
- 10 b) calcium salts of unsubstituted or C₁₋₄-alkyl-substituted benzoic acid,
- c) zinc salts of saturated or unsaturated, linear or branched monocarboxylic acids containing 6 to 36 carbon atoms,
- d) magnesium salts of saturated or unsaturated, linear or branched monocarboxylic acids containing 6 to 36 carbon atoms,
- 15 e) magnesium salts of saturated or unsaturated dicarboxylic acids containing 6 to 10 carbon atoms,
- f) aluminium salts of saturated or unsaturated, linear or branched monocarboxylic acids containing 6 to 36 carbon atoms

are used as **lubricants** or **release agents**.

20 The above-mentioned calcium, magnesium, zinc and aluminium salts may be used both individually and in admixture with one another.

Other lubricants or release agents which may be used individually or in combination with one another are the relevant substances known from the prior art. Compounds of the following types are preferably used:

25 hydrocarbon waxes which melt at temperatures of 70 to 130°C, oxidized polyethylene waxes, free fatty acids containing 8 to 22 carbon atoms and branched-chain isomers thereof, for example stearic acid or even hydroxystearic acid, α -olefins, wax esters, i.e. esters of relatively long-chain monocarboxylic acids and monoalcohols, primary and secondary,

30 saturated and unsaturated higher alcohols preferably containing 16 to 44

carbon atoms in the molecule, ethylenediamine stearate, montanic acid esters of diols, for example of ethanediol, butane-1,3-diol and glycerol, mixtures of such montanic acid esters with nonesterified montanic acids, partial esters of fatty acids containing 8 to 22 carbon atoms and polyols
5 containing 2 to 6 carbon atoms and 2 to 6 hydroxyl groups which contain on average at least one free polyol hydroxyl group per molecule. Also suitable are the mixed esters described in **DE-C-19 07 768** with hydroxyl or acid values of 0 to 6 of aliphatic, cycloaliphatic or aromatic dicarboxylic acids containing 2 to 22 carbon atoms in the molecule, aliphatic polyols
10 containing 2 to 6 hydroxyl groups in the molecule and aliphatic monocarboxylic acids containing 12 to 30 carbon atoms in the molecule. Examples of these mixed esters are mixed esters of maleic acid/pentaerythritol/behenic acid, mixed esters of adipic acid/pentaerythritol/oleic acid and mixed esters of adipic acid/pentaerythritol/stearic acid. According to
15 the invention, corresponding lubricants or release agents may be used both individually and in combination with one another and also in combination with the above-mentioned calcium, magnesium or aluminium salts.

In one embodiment of the invention, compounds selected from the group consisting of talcum, kaolin, chalk and the like, are used as **fillers**.

20 In another embodiment of the invention, compounds selected from the group consisting of calcium and/or zinc soaps, antioxidants, cationic layer compounds, for example hydrotalcites or modified hydrotalcites, zeolites, are used as **heat stabilizers**.

As known to the expert, additives used in the processing of plastics
25 may be classified not only in regard to their function but also in regard to their chemical structure. From the structure perspective, too, the additives according to the invention are not subject to any restrictions. It is pointed out in this connection that compounds belonging to a certain class, i.e. compounds which may be structurally assigned to the same class, often
30 perform not just one but two or more functions in practice. For example,

calcium or zinc soaps - as described above - may act as lubricants and/or release agents but may also be used to improve thermal stability, for example in the processing of polyvinyl chloride (PVC).

The additive granules ("beads") according to the invention are
5 generally **produced** as follows: a composition containing plastic additives, more particularly a composition consisting solely of plastic additives, is introduced into a single-screw or twin-screw extruder. Twin-screw kneader/extruders (twin-screw co-rotating or contra-rotating extruders) are preferred, an extrusion pressure of 15 to 100 bar and more particularly in
10 the range from 25 to 60 bar preferably being established. Basically, the temperature in the extruder is not critical although extrusion is preferably carried out at 20 to 110°C. The extruders used are provided with granulation heads equipped in particular with multiple-bore extrusion dies. The effect of this is that the melt is extruded into fine strands which, after
15 leaving the die, are converted into cylindrical granules by means of a chopping blade. Multiple bore dies with bores between 0.8 and 5 mm and more particularly between 1.5 and 2.5 mm in diameter are preferably used. The chopping temperature is preferably adjusted to a value of 30 to 110°C and more preferably to a value of 40 to 80°C. These granules are then
20 spheronized continuously or in batches in conventional spheronizers. The spheronizing temperature is adjusted so that the granules have sufficient plasticity. The preferred spheronizing temperature is between 20 and 110°C. Relevant spheronizing techniques, especially marumerizing, are known to the expert. Reference is made by way of example in this
25 connection to the disclosure of German patent **DE-C-12 94 351** "Vorrichtung zur Herstellung von kugelförmigen Körnern aus feuchten, vorgeformten Teilchen (arrangement for the production of spherical granules from moist preformed particles)" which describes a spheronizer with a rotating bottom disk, the required degree of spheronizing being
30 adjustable by variation of the residence time of the granules in the

spheronizer and/or the rotational speed of the disk. According to the invention, any commercially available spheronizers may be used.

In one embodiment, the still plastic additive granules initially formed may be impregnated with other active substances before, during or after
5 spheronizing. These other active substances may be, for example, particularly heat-sensitive plastic additives. In one particularly preferred embodiment, the additive granules according to the invention are surface-**powdered** with one or more compounds. Organic active substances, inorganic active substances and release agents, which may be used
10 individually or in combination with one another, are particularly suitable for this purpose. Zeolites and cationic layer lattice compounds, for example hydrotalcites or modified hydrotalcites, are most particularly suitable. The compounds used for powdering are used in particular in quantities of 0.01 to 5% by weight, based on the additive granules (beads). Powdering is
15 preferably carried out at the same time as spheronizing.

As already mentioned, the plastic additive granules ("beads") according to the invention are present in the form of spherical or cylindrical granules with a length-to-diameter ratio of 1:1 to 3:1. In one important
embodiment, particle size and particle shape are uniform. The preferred
20 particle form is spherical. Preferred particle sizes are in the range from 0.5 to 5 mm sphere diameter and more particularly in the range from 0.8 to 3 mm. The constituents of these spheres may correspond in type and quantity to standard formulations for plastic additive compositions.

In another embodiment, the additive granules according to the
25 invention may be recycled. By this is meant that they may be reused together with other substances in the first process step for producing the additive granules - extrusion.

The present invention also relates to **compositions** for the processing of plastics containing additives for the processing of plastics,
30 characterized in that the compositions are present in a granular supply form

and in that the granules are present in the form of spherical or cylindrical granules with a length-to-diameter ratio of 1:1 to 3:1.

The present invention also relates to the **use** of granules as auxiliaries for the processing of plastics, characterized in that the granules
5 consist of one or more typical plastic additives and are present in the form of spherical or cylindrical granules with a length-to-diameter ratio of 1:1 to 3:1.

The present invention also relates to a **process** for the production of plastics, characterized in that powder-form and/or granular thermoplastic
10 homopolymers and/or copolymers are subjected to molding, more particularly extrusion, injection molding or film blowing, together with the additive granules according to the invention. Any of the machines known to the relevant expert may be used, the various commercially available single- and twin-screw extruders being particularly suitable for extrusion.

15

Examples

1. Materials

For the following tests, a commercially available powder-form Ca/Zn stabilizer ("Stabilox CZ 2697", Henkel, Düsseldorf) was processed

- 20
- to rodlet granules (= additive granules intended for comparison) and
 - to spheronized beads (= additives granules according to the invention).

2. Production of the materials

2.1. Rodlet granules

25 A CPM granulator (pressing temperature 30°C) was used to produce the rodlet granules. The rodlets obtained had a diameter of 3 mm and a length of about 5 mm.

2.2. Beads

30 The additive granules according to the invention were produced as

follows: powder-form Stabilox CZ 2697 was continuously added to a twin-screw kneader (Werner & Pfleiderer type ZSK 35 extruder = twin-screw kneader/co-rotating extruder; screw diameter = 25 mm; L/D = 12) of which the housing, including the granulation head of the extruder, was heated to 50°C. The screw speed was 160 r.p.m., the extrusion pressure 42 bar and the specific energy input 0.017 kWh/kg. The melt was extruded through the extruder head multiple-bore die to form fine strands which, after leaving the die, were size-reduced to cylindrical granules by a chopping blade (hot-chopping granulation head with a 47-bore die (bore diameter 2 mm); twin-bladed cutter; chopping temperature 50°C; blade speed 2650 r.p.m.). The granules collecting from the extruder/granulator were spheronized in a commercially available spheronizer of the Marumerizer type (Schlüter RM 400 Spheronizer - spheronizing conditions: rotational speed 320 r.p.m.; residence time 30 s). In the spheronizer, the granules were powdered with 3% by weight - based on the Stabilox CZ 2697 used - of Sasil A 40 (Wessalith P, Degussa AG). The granules were then sieved through a 2.5 mm sieve, about 10% of oversize granules (agglomerates) being removed. The additive granules obtained ("beads") were substantially spherical.

3. Performance tests

3.1. Determination of abrasion

Quantities of 50 g of the rodlet-like and the bead-like Ca/Zn stabilizer (produced as described above in 2.1. and 2.2.) were subjected to mechanical stressing in a Retsch sieve analyzer and the abrasion was determined. The following parameters were adjusted: time 5 mins., vibration amplitude 1 mm, mesh width of test sieve: 0.315 mm.

Abrasion

<i>Supply Form</i>	<i>Abrasion [g]</i>	<i>Abrasion [g]</i>
Rodlet granules 2.1.	0.23	0.46
Beads 2.2.	0.02	0.04

As can be seen from the Table, the beads showed considerably lower abrasion. This is of great importance from the applicational perspective.

3.2. Determination of flowability

To determine flowability, quantities of 96 g of the rodlet granules 2.1. and the beads 2.2. were introduced into a funnel closed at its lower end, the outlet was opened and the outflow time was measured. The funnel (polyethylene powder funnel with an upper diameter of 105 mm) had the following dimensions: diameter of outlet: 23 mm, length of outlet: 23 mm).

Flowability

<i>Supply form</i>	<i>Outflow time [s]</i>
Rodlet granules	2.6 / 3.2 / 2.8
Beads	1.5 / 1.4 / 1.4

The outflow times were measured three times.

As can be seen from the Table, the outflow time was significantly shorter for the beads according to the invention than for the rodlet granules. In practice, this means that flowability is considerably improved, thus ensuring higher feed rates.

3.3 Use in PVC formulations

The performance properties of powder, rodlet granules and beads

were compared using the Ca/Zn stabilizer Stabilox CZ 2697. To this end, the individual supply forms were processed with polyvinyl chloride (PVC, "Evipol SH 6830" = commercially available suspension PVC) in a Herschel mixer to form a dry blend (quantity of material: 3 kg, heating to 120°C, subsequent cooling)

Formulations

	<i>B1</i>	<i>B2</i>	<i>B3</i>
EVIPOL SH 6830	100	100	100
Stabilox CZ 2697 (powder 1.)	3.35	-	-
Stabilox CZ 2697 (rodlet granules 2.1.)	-	3.35	-
Stabilox CZ 2697 (beads 2.2.)	-	-	3.35

Figures in Table = parts by weight

Formulations B1 to B3 (dry blends) were tested first for sieve residue and bulk density:

Sieve residue and bulk density

	<i>Sieve residue [>0.5 mm]</i>	<i>Bulk density</i>
Formulation B1	0.09	621
Formulation B2	0.12	617
Formulation B3	0.07	614

Sieve residue: expressed in g based on 200 g of dry blend

Bulk density: expressed in g/l

Explanation of the determination of the sieve residue: as an indicator of the degree of dispersion during mixing, 200 g of the dry blend

were sieved through a 0.5 mm mesh sieve. All the particles above 0.5 mm in size remain in the sieve in this test. This is known as the sieve residue.

The dry blends were then extruded to a flat strip in a Weber twin-screw extruder. The extrusion parameters were as follows: screw speed 20 r.p.m., machine load 42, temperature 180°C. The strip had a thickness of 1.5 mm and a width of 25 mm.

The color of the strips was determined immediately after their production (so-called initial color) using the L^*, a^*, b^* method known to the expert (cf. DIN 6174, CIELAB 1976). The b^* value indicates the position on the blue/yellow axis. Normally, the b^* value is also called the yellow value. A commercially available instrument known as a "Micro Color" (Dr. Lange) was used for the measurements. The color values are set out in the following Table. Another parameter determined was how long it took the test strips to turn black in color during heat treatment in a "thermo-oven" (cf. DIN 5033). To this end, the strips were heated at 180°C in a thermo-oven, being briefly removed from the oven every 15 minutes for visual examination. The time in minutes which the strips took to turn black is termed "long-term stability". The test results are set out in the following Table.

Heat stability

	Yellow value b^* after		Long term stability (= end of stability after)
	0 mins.	15 mins.	
Formulation B1	15	34	90 mins
Formulation B2	15	35	90 mins.
Formulation B3	15	35	90 mins.

Overall, it was found that the strip which had been produced using

the beads according to the invention (formulation B3) was as heat-stable as the strips which had been produced using powder or rodlet granules (formulations B1 and B2). Accordingly, the above-mentioned performance-related advantages of the additive granules according to the invention

5 ("beads"), i.e. in particular less dust, better flowability, greater formulation flexibility, have no adverse effects on their ability to heat-stabilize PVC.